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Introduction

In the last decade, graphene and graphene oxide (GO) have been intensively investigated due to their excellent electronic, optical, mechanical, thermal properties and their wide range of applications such as electronic and energy storage devices, optical materials, biosensors and water treatment.

GO is single-atom carbon layer containing range of reactive oxygen groups upon which its structure and properties directly depend. Nevertheless, large-scale production of high quality GO is still a challenging task for researchers and since industrial-scale chemical synthesis of GO are inherently generating large amount of toxic waste, it is more than necessary to find a new, cleaner and cheaper way of its production. [1]

However, mechanochemistry is becoming more disseminated as a technique because it can promote reactions between solids, with either no added solvent or only minimal amounts. Moreover, it offers more sustainable, environmental friendly and energy-facilitated synthesis pathways, which could be the way to reduce or completely remove our current dependence on solvents in GO production. [2]

Herein, we present versatile and eco-friendly approach for mechanochemical preparation of GO.

Furthermore, we also present it is possible to obtain 3D graphene hydro- (GHs) and aerogels (GAs) via one-step hydrothermal method using mechanochemically prepared GO. GHs are a new class of 3D carbon monoliths holding promise for applications as diverse as electrochemical energy storage, tissue engineering, CO₂ capture and pollutant adsorption. They consist of entangled layers of graphene, albeit they partially retain the excellent properties of monolayer graphene. [3]

Methodology

Initially, different amount of graphite flakes, H₂SO₄ and KMnO₄ were mixed for all samples and mechanochemically treated in planetary ball mill using different reaction parameters as shown in Table 1 and 2. Furthermore, GO1 was milled 3 times for 1h with 10 min pause in between, while GO2 and GO3 were milled for 3,5h with 10 min of milling and 10 min of pause in between.

Products of the mechanochemical treatment were washed with the HCL (10%) and with deionized water until forming a stable suspension (graphite oxide) and then treated in an ultrasound washer for 1h to obtain GO dispersions, which were additionally purified by dialysis for 2 days for removal of inorganic ions.

Table 1. Chemicals used in synthesis process

Chemicals	Producer
graphite, x > 400 μm	Graphenea
KMnO ₄	E. Merch
H ₂ SO ₄ (87%)	Kemika
HCl (10%)	VWR
deionized water	-

Table 2. Reaction conditions for synthesis of GO

sample	jar / balls	amount	diameter (mm)	m _{powder} : m _{ball}	rpm	reaction time (h)	γ (mg/ml)	G : H ₂ SO ₄ : KMnO ₄
GO1	ZrO ₂ /ZrO ₂	7	12	1:20	500	3	1.21	1 : 3.2 : 4.4
GO2	ZrO ₂ /ZrO ₂	7	12	1:20	500	3.5	3.87	1 : 4 : 5.7
GO3	ZrO ₂ /ZrO ₂	15	10	1:19.5	500	3.5	6.51	1 : 5 : 7

Table 3. Reaction conditions for hydrothermal synthesis of graphene hydrogels (GHs)

sample	γ (mg/ml)	V (ml)	reaction time (h)	T (°C)
rGO1	4	4	3	180
rGO2	4.37	4.5	16	180
rGO3	6.86	4.5	16	180

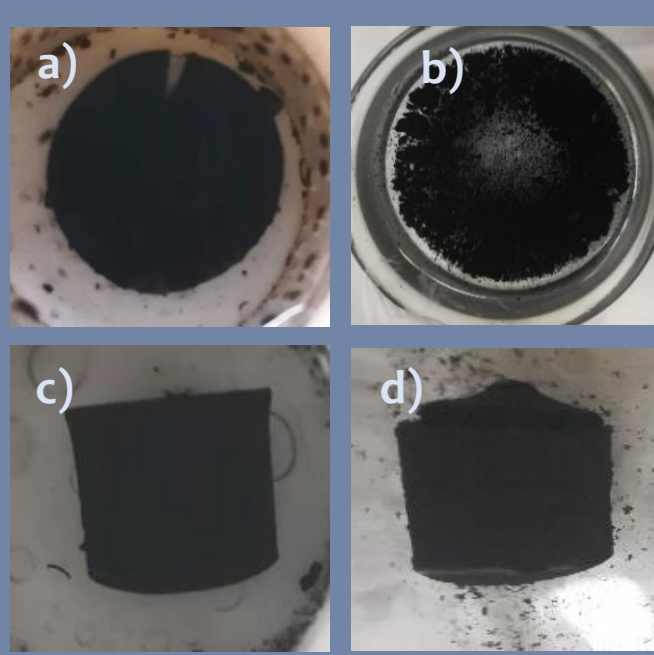
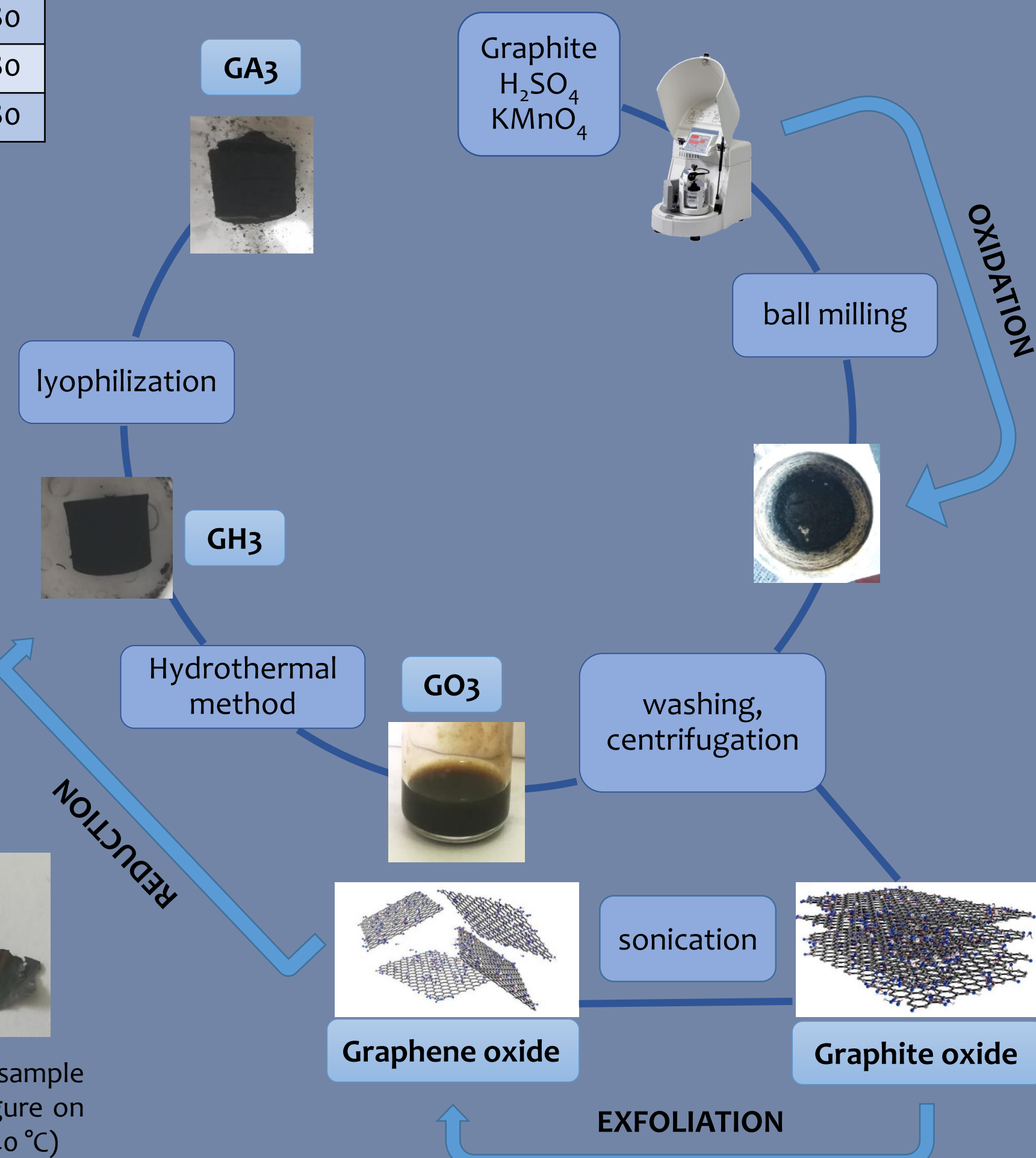


Figure 1. Photographs of graphene hydrogels after hydrothermal reduction: a) rGO2 in autoclave and b) after applying a small force on it; c) rGO3 in autoclave and d) obtained graphene aerogel (GA3) after a freeze-drying step



Figure 2. On the left is shown synthesized sample GO3 and commercial GO from Graphenea. Figure on the right represents dry GO3 (vacuum oven, 40 °C)

Mechanochemical synthesis of GO



Results

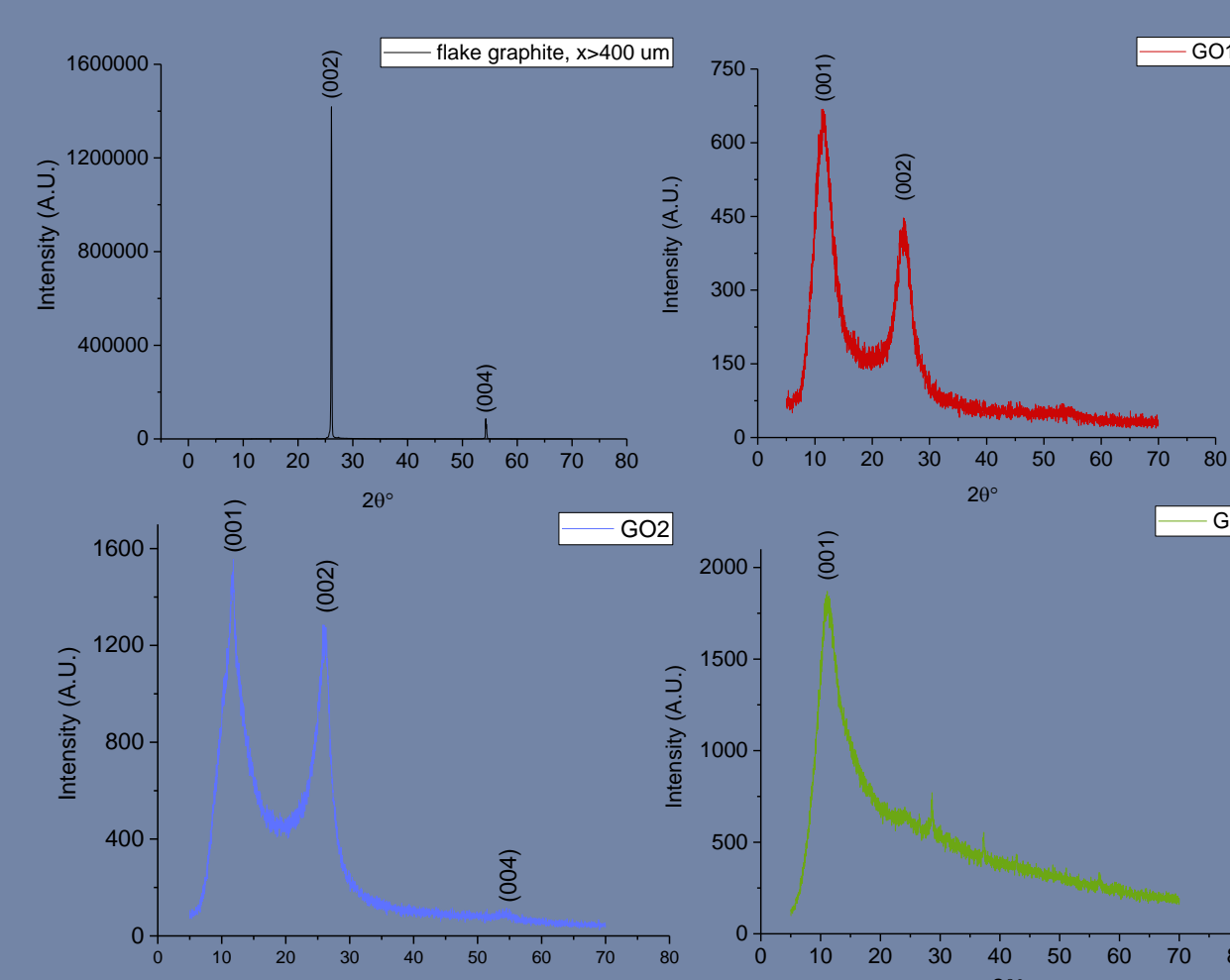


Figure 3. XRD pattern of flake graphite used for GO synthesis and samples GO1, GO2 and GO3

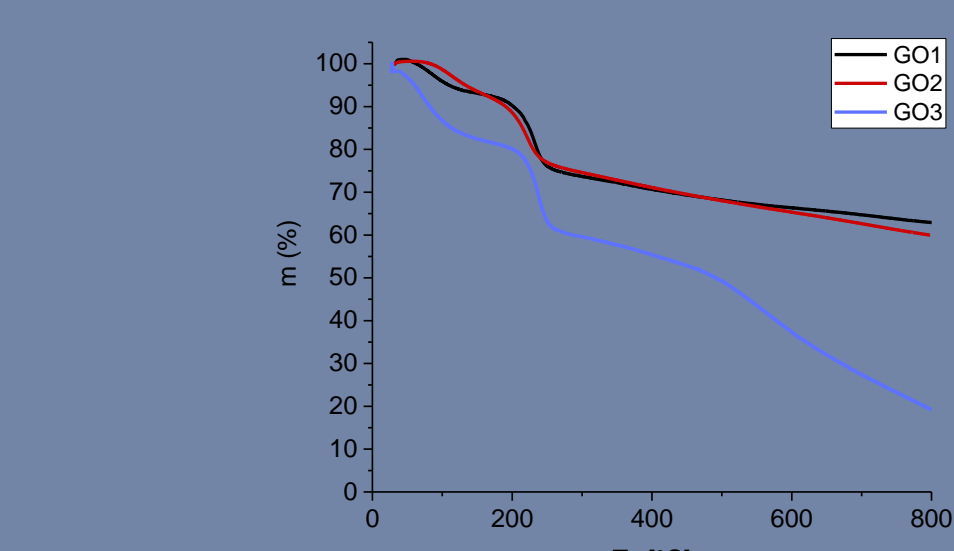


Figure 4. TG curves for samples GO1, GO2 and GO3

Table 4. Observed 2θ values and corresponding interplanar spacing of graphite and all measured samples

Sample	2θ°	2θ°	d ₁ / Å	d ₂ / Å
graphite	26.09	-	3.41	-
GO1	11.45	25.54	7.72	3.49
GO2	11.72	25.94	7.55	3.43
GO3	11.32	-	7.81	-

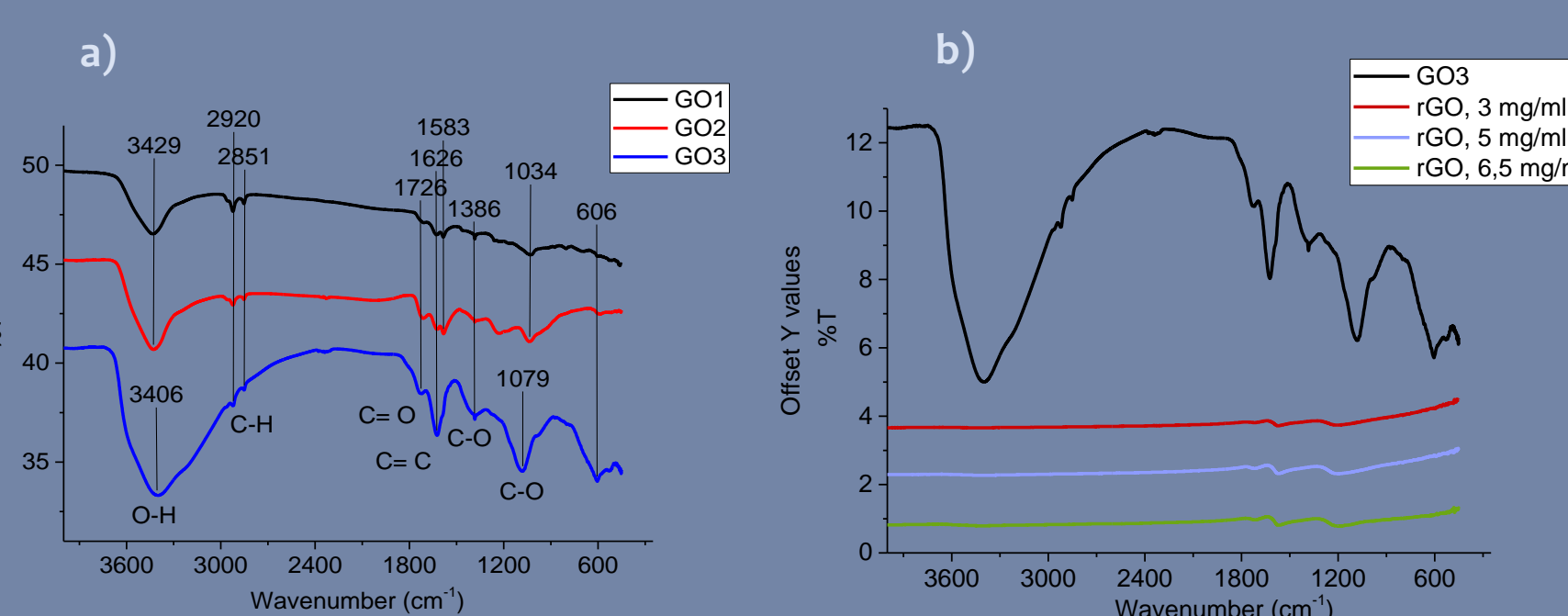


Figure 5. FT-IR spectra for samples a) GO1, GO2, GO3 and b) FT-IR spectra of GO3 and reduced GAs samples (rGO3)

Table 5. Summary of weight loss (Δm%) of the samples GO1, GO2 and GO3, under N₂ atmosphere using TGA

Sample	Δm [%] (30-160 °C)	Δm [%] (160-300 °C)	Δm [%] (300-600 °C)	Δm [%] (600-800 °C)	degree of oxidation
GO1	7	19	8	3	30
GO2	7	18	10	5	33
GO3	18	22	23	18	63

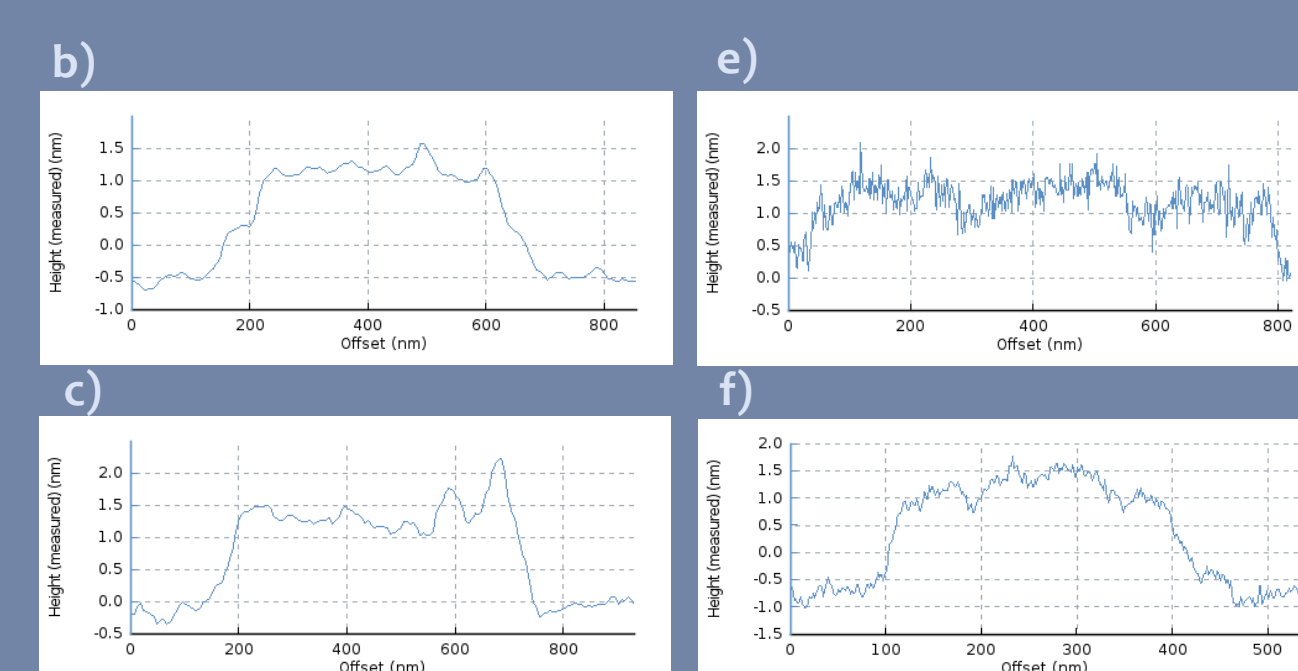
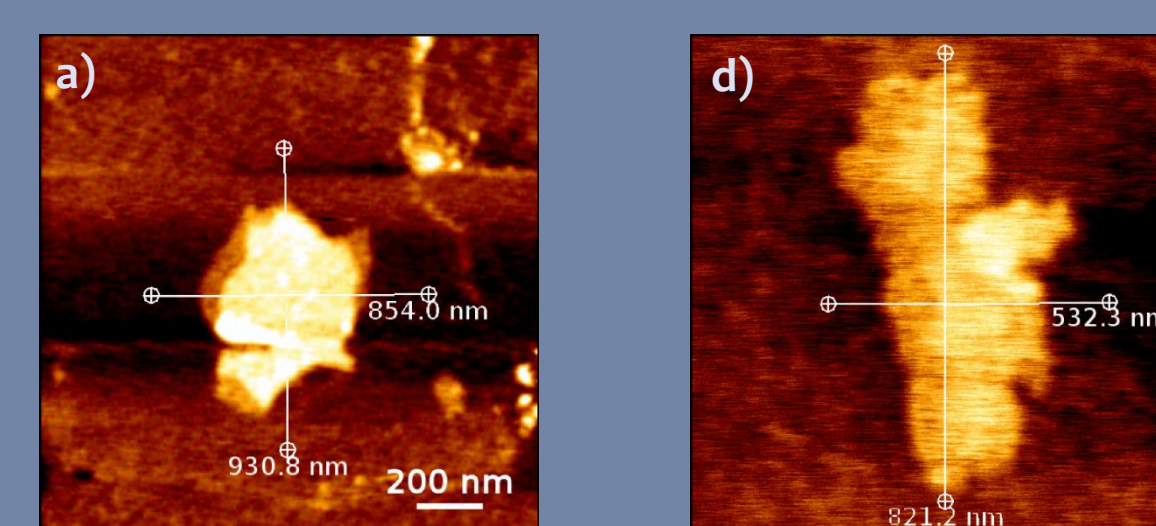


Figure 6. AFM image of sample GO3 and corresponding cross-section analysis of width (b) and height (c) profile. AFM image of rGO3 and its corresponding cross-section analysis width (e) and height (f) profile

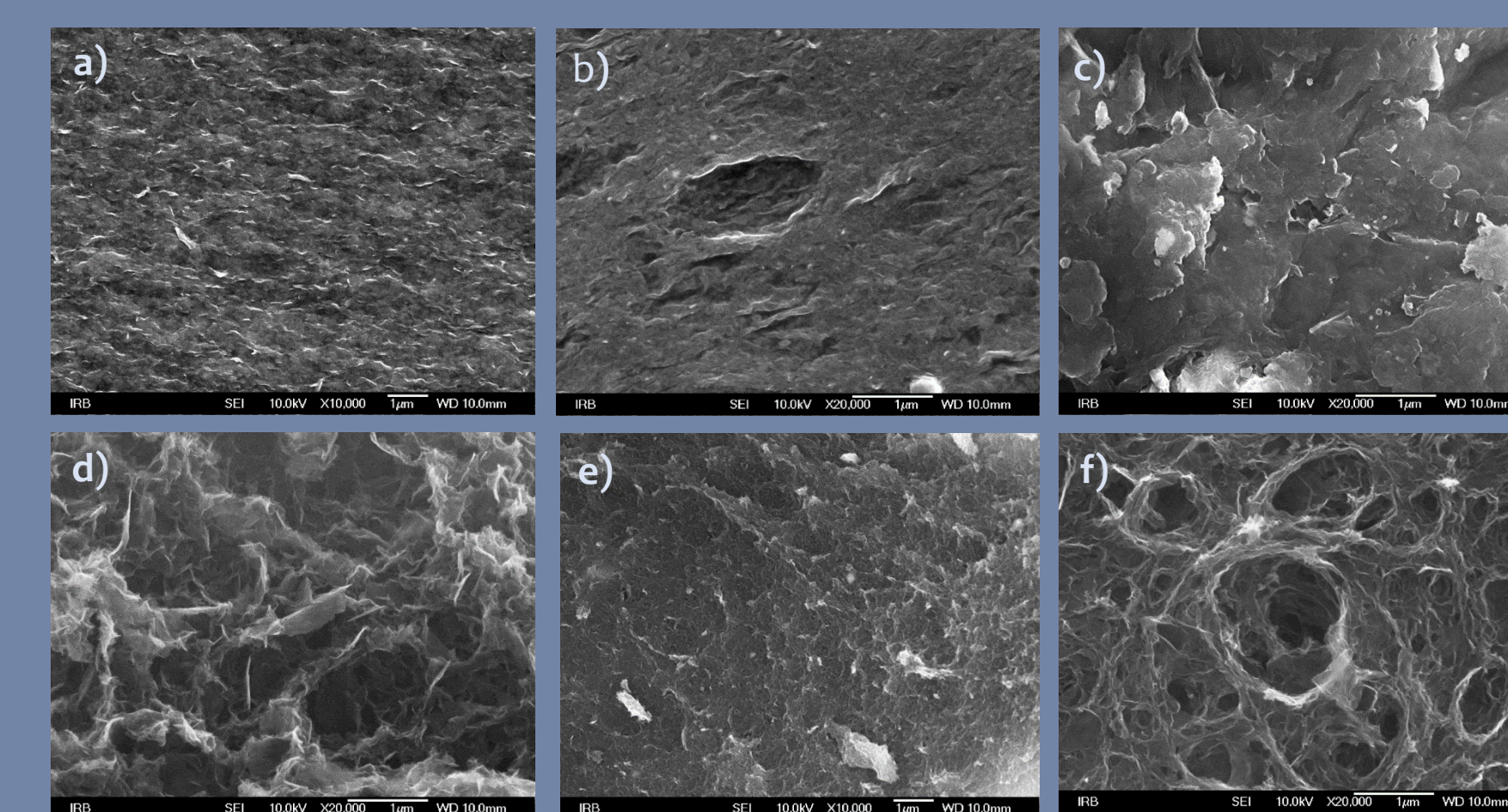


Figure 7. SEM image for samples a) GO1, b) GO2, c) GO3 and obtained graphene hydrogels (GHs): d) rGO1, e) rGO2 and f) rGO3

Conclusion

- XRD analysis shows that with increasing oxidation levels of GO, the intensity of the peak at 26° decreases and for GO3 disappears entirely pointing to a better quality of GO. Mechanochemical synthesis resulted with GO having an interlayer distance of 7.55–7.81 Å.
- TGA shows that obtained samples contain 30–63% of oxygen, where GO3 unlike other samples contains a higher amount of lactone, phenol and ether groups. Presence of different oxygen functionalities and successful reduction of all samples are confirmed with FT-IR spectroscopy, respectively.
- SEM analysis shows morphology of all samples corresponding to the literature GO morphology. GO2 is most, while GO3 is least agglomerated.
- The single layer GO and single layer rGO is proven by AFM cross-section analysis suggesting good quality of the sample. Particle size SEM analysis corresponds to AFM measurements.
- It is possible to mechanochemically prepare GO, mitigate the explosive nature of the reaction mixture and eliminate emission of toxic gases by using minimal amount of oxidising reactants, as well as to reduce the reaction time from 2-3 weeks to 3-4 days.
- Quality of the as synthesized GO is good enough for preparing graphene 3D frameworks
- Future work will focus on simultaneous control and engineer the porosity and morphology of the graphene frameworks and its composites, as well as finding different intercalating agents and oxidants for solvent-free GO synthesis

Reference

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